

Evaluation of selected static methods used to estimate element mobility, acid-generating and acid-neutralizing potentials associated with geologically diverse mining wastes



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ABSTRACT

A comparison study of selected static leaching and acid–base accounting (ABA) methods using a mineralogically diverse set of 12 modern-style, metal mine waste samples was undertaken to understand the relative performance of the various tests. To complement this study, in-depth mineralogical studies were conducted in order to elucidate the relationships between sample mineralogy, weathering features, and leachate and ABA characteristics. In part one of the study, splits of the samples were leached using six commonly used leaching tests including paste pH, the U.S. Geological Survey (USGS) Field Leach Test (FLT) (both 5-min and 18-h agitation), the U.S. Environmental Protection Agency (USEPA) Method 1312 SPLP (both leachate pH 4.2 and leachate pH 5.0), and the USEPA Method 1311 TCLP (leachate pH 4.9). Leachate geochemical trends were compared in order to assess differences, if any, produced by the various leaching procedures. Results showed that the FLT (5-min agitation) was just as effective as the 18-h leaching tests in revealing the leachate geochemical characteristics of the samples. Leaching results also showed that the TCLP leaching test produces inconsistent results when compared to results produced from the other leaching tests. In part two of the study, the ABA was determined on splits of the samples using both well-established traditional static testing methods and a relatively quick, simplified net acid–base accounting (NABA) procedure. Results showed that the traditional methods, while time consuming, provide the most in-depth data on both the acid generating, and acid neutralizing tendencies of the samples. However, the simplified NABA method provided a relatively fast, effective estimation of the net acid–base account of the samples. Overall, this study showed that while most of the well-established methods are useful and effective, the use of a simplified leaching test and the NABA acid–base accounting method provide investigators fast, quantitative tools that can be used to provide rapid, reliable information about the leachability of metals and other constituents of concern, and the acid-generating potential of metal mining waste.

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Abbreviations: ABA, acid–base account; AMD, acid mine drainage; AP, acid-generating potential; CVAFS, continuous flow-cold-vapor-atomic fluorescence spectrometry; DI, deionized; FLT, Field Leach Test; IC, Ion chromatography; ICP-AES, inductively coupled plasma-atomic emission spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; MIW, mining impacted water; NABA, net acid–base account; NNP, net-neutralization potential; NP, neutralizing potential; NPR, neutralization potential ratio; SEM, scanning electron microscope; SPLP, synthetic precipitation leaching procedure; TCLP, toxicity characteristic leaching procedure; USEPA, U.S. Environmental Protection Agency; USGS, U.S. Geological Survey; XRD, X-ray diffraction analysis.

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1. Introduction

Mining impacted water (MIW) is a major concern for metal-mining operations. MIW results from the oxidative weathering of sulfide minerals, principally pyrite or pyrrhotite, in waste rock, mill tailings, pit walls, and mine workings. MIW can cause a host of environmental problems because low pH waters have the ability to dissolve and transport metals and other constituents. However, the solubility of metals, and other contaminants vary with pH. Cationic species, such as Cu, Pb, Zn, Cd, Ni, and Co, are more soluble at low pH. In contrast, elements that form anionic species, such as As, Sb, Se, Cr, V, and Mo, tend to be more soluble at high pH. Thus, the acid-generating potential of mining waste greatly influences the composition, transport, and fate of contaminants mobilized from mining waste.

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Ultimately, mineralogy and weathering determine and control the potential for a mine waste to be a generator or a neutralizer of acid (Plumlee and Logsdon, 1999; Seal and Hammarstrom, 2003; Maest et al., 2005). Mechanical, chemical, and biologic weathering processes result in the breakdown and reaction of minerals, and if climatic and mineralogical conditions are conducive, weathering results in the formation of end-member, readily soluble, hydrated weathering salts like those shown in Fig. 1(a).

Secondary salts such as these represent the end product (sum) of all of the geochemical and acid–base reactions that have taken place in the mine waste over time. The salts play a key role in moving acid and metals from the mine waste into the environment because they serve as sinks that control the characteristics and constituents of leachate that will be generated from the waste upon exposure to water.

The risk of acid generation and metal mobility can be assessed and characterized through a series of tests that fall into two broad categories: static tests and kinetic tests. Static tests, the subject of this paper, comprise a single test or set of tests performed on mining waste at a single time. In contrast, kinetic tests consist of continuous or intermittent leaching for extended periods, sometimes spanning months to years, and are sampled on a periodic basis, such as weekly. Static tests can be further divided into leaching tests and acid–base accounting (ABA) studies. Static testing methods are well established and widely accepted and a general overview of static leaching and ABA methods are found in INAP (2009), Maest et al. (2005), and Lapakko (2002).

While numerous studies have compared the use of several static tests at specific sample sites (i.e. Lei and Watkins (2005) and Lengke et al. (2010)). The primary goal of our study is to compare several different static tests on a suite of modern mine waste samples that span a diversity of mineralogical and geochemical compositions in order to assess and compare results produced by both traditional and simplified static methods. Results produced from this study help constrain, correlate, and verify the relationship between leaching, mineralogy, and the net acid–base account of the samples.

2. Samples included in this study

The samples included in this study represent modern-style mine waste, meaning that, although some samples are from abandoned or inactive mines, all of the ore was processed using methods currently in use. The samples represent diverse base and precious metal mineral deposit types and the samples include a range of mineralogical and geochemical, characteristics (Table 1).

Previous mineralogical studies showed that the mine waste samples are of mixed sulfide mineralogy, containing varying amounts of pyrrhotite, pyrite, chalcocopyrite, sphalerite, galena, and arsenopyrite, and are potential repositories for acid-generating potential and metal contaminants (Piatak et al., 2007). A number of the samples also contained varying amounts of carbonate minerals. All the samples except (NZ-A) were collected from the oxidized surface of the mine waste piles. The (NZ-A) sample was collected from mostly un-oxidized mill tailings.

3. Methods

3.1. Sample preparation

After collection, bulk samples were dried in ambient air and then homogenized. The samples were then dry-sieved to pass a –10 mesh (2-mm) stainless steel screen and the <2 (mm) fraction was used for study.

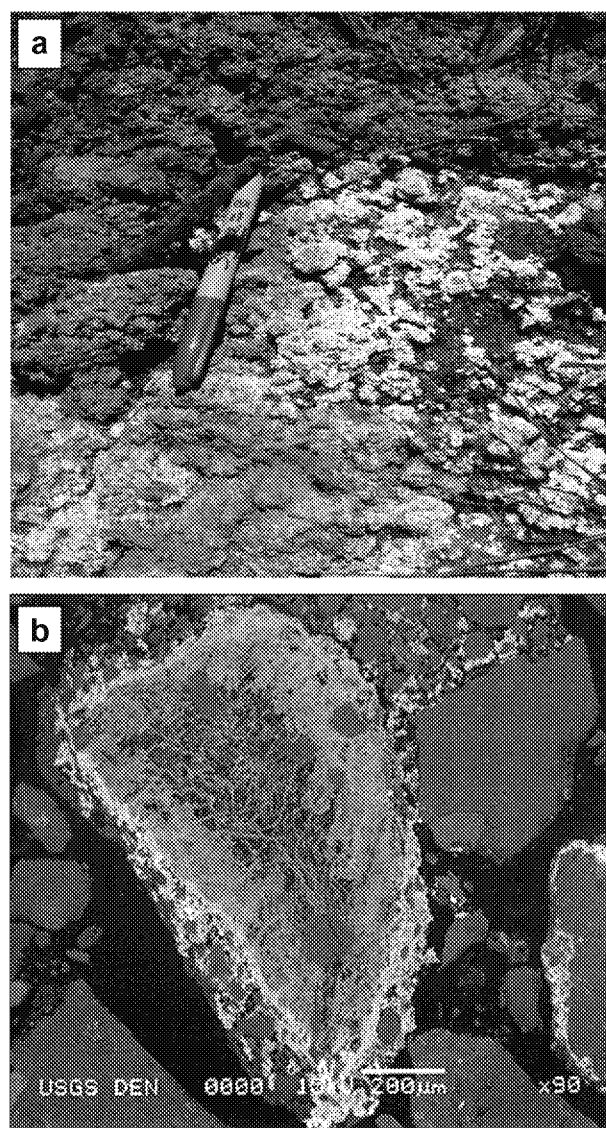


Fig. 1. (a) Photograph of typical, readily soluble secondary salts (white areas) forming on the surface of metal mining waste. These weathering salts represent the “sum” of all the geochemical reactions that have taken place in the mine waste over time. (b) Scanning electron microscope (SEM) photomicrograph showing weathered sphalerite (ZnS) grain from processed metal-mine waste material. Mineralogy studies showed that the grain has undergone advanced oxidation, dissolution etching, and alteration to iron oxides and readily soluble secondary sulfate salts (bright white coatings).

3.2. Mineralogy

Previous studies of metal mine waste have shown that micro-mineralogical and micro-structural controls (Diehl et al., 2005, 2006, 2007, 2008) influence both the net acid–base account and the leaching potential of water-soluble constituents. In order to highlight these processes, we conducted extensive mineralogical characterization on sample splits from this study using transmitted- and reflected-light microscopy, scanning electron microscope (SEM) and electron microprobe in combination with X-ray diffraction (XRD). In addition, thin sections and bulk grain samples were studied to determine mineralogy, provide qualitative minor- to trace-element content and residence, textures, and microstructures such as micro-veining, micro-faulting, and lattice defects. Sulfide grains from mine waste were examined specifically to search for readily soluble metal-bearing phases like those shown

Table 1

Location and selected characteristics of modern style metal-mine waste samples included in this study [sulfide and carbonate content from Piatak et al. (2007)].

Locality and sample ID (in parentheses)	Deposit type/commodity	Sample type	Sulfide content	Carbonate content
Elizabeth mine, Vermont (TP1-N, TP1-S)	Siliciclastic–mafic massive sulfide hosted in schists, amphibolites [Cu]	<2 mm mine waste composite	High	Low
Callahan mine, Maine (USGS-CLTPC, USGS-CLTPF, CLHN-TP-2)	Felsic–siliciclastic massive sulfide hosted in volcanics [Zn, Cu, Pb, Ag]	<2 mm mine waste composite	High	High
Martha mine, New Zealand (NZ-A)	Low-sulfidation epithermal vein deposit hosted in volcanic rocks [Au, Ag]	<2 mm mill tailings composite	Low	Low
Anvil-Faro, Yukon, Canada	Sedimentary exhalative (sedex) massive sulfide deposit [Pb, Zn, Ag]	<2 mm mine waste composite	High	Low
Giant mine, Northwest Territories, Canada (Giant N.W., Giant N., Giant Central, and Giant S.)	Orogenic gold deposit hosted by metavolcanic rocks [Au]	<2 mm mine waste composite	Low	Moderate to high
Ptarmigan mine, Northwest Territories, Canada	Orogenic gold deposit hosted by metaturbidites [Au]	<2 mm mine waste composite	Low	Moderate to high

in Fig. 1(b). Selected samples were characterized using digital element intensity maps produced using the SEM.

3.3. Leaching studies

For the leaching study, we used six batch leaching tests, including tests that have been used for regulatory and non-regulatory purposes. The samples were leached using specific leachant chemistry, leaching ratios, agitation methods, and equipment (Table 2).

Following are highlights for each test.

- The Paste pH test has traditionally been used as a screening test to quickly determine if mine waste samples produce acidic, neutral, or alkaline slurries when mixed with deionized (DI) water (Price et al., 1997; White et al., 1999). The downside of this test is that further characterization of the slurry/leachate is not possible because the paste pH test does not produce enough leachate for analysis.
- The USGS Field Leach Test (FLT) uses deionized water and a 5-min agitation period to quickly assess the readily soluble, water reactive characteristics of a sample (Hageman, 2007). The FLT was originally designed for rapid characterization of metal-mine waste and the procedure was first described in Hageman and Briggs (2000). Since its inception, use of the FLT has expanded, and it is now used in diverse studies to characterize a wide range of other earth materials (Hageman, 2005; Plumlee et al., 2013). An important feature of the FLT is that it uses a 20:1 leaching ratio (leachant/solid). This helps prevent solute saturation and provides enough leachate to complete all the desired analyses. Use of this ratio also allows FLT leachate

geochemical results to be directly compared to results produced from the USEPA Method 1311 (TCLP), and Method 1312 (SPLP) because all three procedures use the same leaching ratio. As part of this study, the 18-h FLT was also used; the 18-h agitation used in this test is equivalent to the agitation period required by the TCLP and SPLP protocols. The 18-h FLT uses the same methodology and apparatus as the 5-min FLT, with the only difference being the length of agitation.

- The U.S. Environmental Protection Agency (USEPA) Method 1312, Synthetic Precipitation Leaching Procedure (SPLP) (USEPA, 2004a) has been used both in regulatory and more commonly in non-regulatory leaching studies. The SPLP is used to characterize the water-soluble, water reactive constituents that are released from samples that have been subject to end-over-end agitation for 18 h. The standard SPLP requires crushing the samples to pass a 9.5-mm sieve, and requires a 20:1 (leachant/solid) leaching ratio. It calls for the use of slightly acidified extraction fluids that were designed to simulate acid rain. Extraction fluid 1 (pH of 4.2 ± 0.05) is to be used in studies of sites east of the Mississippi River (USA). Extraction fluid 2 (pH of 5.0 ± 0.05) is designed for use in studies of samples from sites west of the Mississippi River. For this study, all the mine waste samples were leached using both the pH 4.2 and pH 5.0 leachants. A modified version of the SPLP was used in this study and leaching parameters are provided in Table 2.
- The U.S. Environmental Protection Agency (USEPA) Method 1311 Toxicity Characteristic Leaching Procedure (TCLP) (USEPA, 2004b) is probably the most commonly used regulatory leaching test. The procedure is designed to simulate the worst-case scenario of co-disposal in municipal landfills (Al-Abed

Table 2

Comparison of parameters for the static leaching tests used in this study. Tests include: the U.S. Geological Survey (USGS) Field Leach Test (FLT) (both 5-min and 18-h agitation) and modified versions of the U.S. Environmental Protection Agency (USEPA) Method 1312 (SPLP) (both pH 4.2 and pH 5.0 leachates), and the USEPA Method 1311 (TCLP).

Characteristic	Paste pH	USGS FLT (both 5-min and 18-h agitation)	Modified USEPA 1312 SPLP (both pH 4.2 and pH 5.0 leachates)	Modified USEPA 1311 TCLP
Test type	Batch	Batch	Batch	Batch
Leachate to solid ratio	1:1	20:1	20:1	20:1
Leachate composition	Deionized water	Deionized water	60/40 H ₂ SO ₄ /HNO ₃	Acetic acid/acetate buffer
Leachate pH	~5.7	~5.7	Both 4.2 and 5.0	~4.90
Particle size used	<2 mm	<2 mm	<2 mm	<2 mm
Sample mass/leachate volume	10 g/10 mL	50 g/1 L	100 g/2 L	100 g/2 L
Duration of agitation	<1 min	Both 5 min, and 18 h	18 h	18 h
Agitation method	Stir with glass rod	Hand or mechanically shaken	End-over-end rotary	End-over-end rotary
Filtration	Not applicable	Syringe	Syringe	Syringe
Filter type	Not applicable	Nitrocellulose	Nitrocellulose	Nitrocellulose
Filter pore size	Not applicable	0.45 µm	0.45 µm	0.45 µm

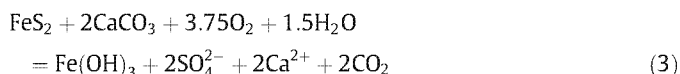
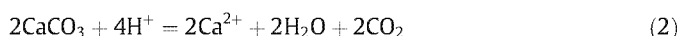
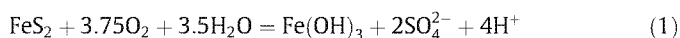
et al., 2005). The standard TCLP calls for crushing the sample to pass a 9.5-mm screen, a 20:1 leaching ratio, and 18-h end-over-end agitation. The primary difference between this test and the SPLP is that this method requires the use of a buffered acetic acid solution ($\text{pH } 4.93 \pm 0.05$) as the leachant. Over time, the TCLP has proven to have significant limitations (USEPA, 1995, 1999; Lackovic et al., 1997; Kosson et al., 2002; Al-Abed et al., 2005) if it is used to assess the “general” leachability of a material. Incorrect use of the TCLP can lead to inaccurate characterization of a sample because this test fails to accurately mimic the leaching process that occurs in the natural environment. Our modifications to the standard TCLP were the same as those listed for the SPLP and are provided in Table 2.

3.4. Leachate analysis

After agitation, the leachates were filtered, and analyzed using similar procedures, equipment, methodology, and instrumentation. Leachate pH was determined on unfiltered aliquots of leachate using a handheld Orion pH meter fitted with an epoxy combination electrode. Specific conductance (SC) was measured on separate unfiltered aliquots of leachate using a hand-held Myron L Model DC4 conductivity meter. Other portions of leachate were then filtered using 60-mL syringes and 0.45- μm pore-size, nitrocellulose capsule filters. If filtration was difficult, a 0.70- μm glass fiber pre-filter was used in series with the 0.45- μm filter. Approximately 20 mL of each filtrate was collected in acid-washed HDPE bottles and preserved by acidification with two drops of ultra-pure nitric acid (HNO_3). Determination of major, minor and trace elements, and sulfate was achieved using inductively coupled plasma-mass spectrometry (ICP-MS) (Lamothe et al., 2002). Standard U.S. Geological Survey (USGS) quality control protocols were used for all analyses and quality assurance, quality control data (QA/QC) for the leaching studies are provided in Supplementary information (SI) Table 1.

3.5. Acid–base accounting

Traditional ABA methods are important geochemical tools. They have proven to be reliable methods for estimation of the potential of a geologic material to produce or consume acid when exposed to the weathering process. ABA is commonly used as a screening tool and is a prerequisite to more intensive kinetic tests. The traditional ABA methods used for this study are based on Sobek et al. (1978) and White et al. (1999) and are based on the following reactions:



These reactions are examples of the chemical balance between acid-generating and acid-neutralizing reactions. Reaction (1) depicts an acid-generating reaction, reaction (2) is an acid-neutralizing reaction, and (3) is a “net-neutral” reaction where the acid-generating potential is balanced by the acid-neutralizing potential. This hypothetical framework forms the basis of acid–base accounting.

Using traditional methods, ABA is determined by quantification of the net-neutralization potential (NNP), which is the difference between the neutralization potential (NP) and the acid-generating potential (AP) of the sample ($\text{NNP} = \text{NP} - \text{AP}$). The NP and AP data are evaluated in different ways. The determination of AP is based on sulfur species (sum of total sulfur/sulfide or sulfur/sulfate) using the LECO elemental analyzer with or without chemical

extractions. The acid-neutralizing potential (NP) is based on wet chemical titration or carbon species determinations using the LECO elemental analyzer with or without chemical extractions. For this study, samples with an NNP of less than 0 are considered to be “potentially acid generating.” Results are reported as kilograms calcium carbonate per metric ton of mine waste ($\text{kg CaCO}_3/\text{t}$).

One of the goals of this study was to evaluate the usefulness and limitations of a simplified method to provide the “net” acid base account (NABA) of the metal mine waste samples. Net, in this case, simply means quantification of whether a mine waste sample is likely to produce acidic, neutral, or alkaline runoff when exposed to natural precipitation. The simplified method used in this study is a modification to a method used by Fey et al. (2000) and is based on the net acid generation (NAG) procedure first described by Lapakko and Lawrence (1993). The primary advantage of this method is that it reacts and accounts for both the acid-producing and acid-neutralizing potential of the sample using one test. This is possible because according to the digestion kinetics of this procedure, the hydrogen peroxide (H_2O_2) rapidly oxidizes sulfides present in the sample thereby forming sulfuric acid (H_2SO_4), which in turn reacts with any acid neutralizing minerals that may be present in the sample. In theory, upon completion of all the reactions, the resulting digestate represents a sum of all of the acid-producing and acid-neutralizing potential of the sample. The value of this test is that it identifies the samples that are not only net-acidic but more specifically quantifies the samples with greater or lesser potential to produce acid. The disadvantage of the test is that it does not quantify which samples have greater or lesser potential to neutralize acid, but only determines the samples that are net-neutralizing. For many purposes, determination of the exact neutralization potential is not as critical because samples that are net-neutralizing generally have less potential to produce negative effects in the environment. In order to conduct the NABA procedure, 1.0 g of prepared (finely ground) sample was weighed into a 250-mL Erlenmeyer glass flask. A total of 150 mL 30% H_2O_2 was added to the sample in three steps. First, 50 mL was slowly added to the sample (this procedure must be done in a hood as it often produces an exothermic reaction and the evolution of vapor). After all reaction ceased, another 50 mL was added, and the flask was swirled. Again, the reaction was allowed to go to completion. The final 50 mL was then added and the flasks were swirled and placed on a hotplate and heated at 90 °C. The samples remained on the hotplate until the reaction was complete. The flasks were then removed from the hotplate and allowed to cool for 15 min. After cooling, 1 mL copper nitrate (CuNO_3) was added and the contents are again swirled. The flask was then placed back on the hotplate and brought to boil (~110 °C). After 10 min, the flask was removed from the hotplate. When cooled to room temperature, the liquid was filtered into a clean 250 mL glass beaker to remove the solids. As a final step, the solids retained in the filter were gently rinsed with 1 M calcium chloride (CaCl_2). Following filtration, the pH of the filtrate was measured and recorded. If the digestate had a $\text{pH} > 7.0$, the solution was not titrated as the sample is considered to be net-neutralizing. If the $\text{pH} < 7.0$, the filtrate was titrated with 0.1 N sodium hydroxide (NaOH). To do this, a stir bar was placed in the beaker and the digestate is constantly stirred during titration. A pH electrode was suspended in the beaker during titration and solution pH was constantly monitored. When the solution pH reached 7.0, the quantity of NaOH consumed during the titration was recorded for calculation. Final NABA was determined by multiplying the number of mL NaOH consumed by the titrant concentration (0.1). The sum was then multiplied by 50. Data were reported in kilograms calcium carbonate (CaCO_3) equivalent required to neutralize 1 metric ton of sample waste ($\text{kg CaCO}_3/\text{t}$). After calculation, a NABA value greater than 0 was considered to be potentially acid generating.

4. Leaching results

We provide and discuss selected leachate parameters and characteristics for all 12 mine waste samples. Complete leachate chemical results (ICP-MS) for all the leaching tests are provided in SI Table 2.

4.1. Leachate pH

The pH was determined on all the leachates immediately following the agitation period and the leachate pH trend for all 12 samples using six leaching tests are shown in Fig. 2(a).

The leachate pH data show that in general, the paste pH, FLT 5-min, FLT 18-h, SPLP pH 4.2, and SPLP pH 5.0 leaching tests produce a similar pH trend for all of the samples except ptarmigan (FLT 5-min) (Fig. 2(a)). However, the pH data produced using the TCLP leaching test did not conform to this trend. It is evident that pH in the TCLP leachates was controlled primarily by the acetic acid in the raw TCLP leachant and not by the soluble acid or alkaline components leached from the samples. This resulted in the acetic acid overwhelming most of the acid buffering capacity of the samples, falsely indicating that several of the mine wastes produced circum-neutral to slightly acidic pH when the other leaching tests showed that they actually produced neutral to alkaline pH. The failure of the TCLP to provide relative leachate pH data shows a limitation of the TCLP, and suggests that this test should not be used to assess or characterize the potential of a metal-mining waste to produce acidic or alkaline leachate. The pH results from the other leaching tests showed that circum-neutral to acidic leachate was produced from the TP1-N, TP1-S and the Anvil-Faro mining wastes, all of which had high sulfide and low carbonate mineralogy. Circum-neutral to slightly alkaline leachate was produced by all the other mining wastes. The NZ-A mining waste produced the highest leachate pH (FLT 5-min, 9.80). Other observations included the finding that DI water was just as effective as either of the slightly acidified USEPA 1312 (pH 4.20 and pH 5.0) leachants in identifying the leachate pH of the mining wastes. Also, agitation time did not make a significant difference for 11 of the 12 samples and the 5-min FLT, and the 1-h paste pH tests produced pH values that were similar to those produced by the 18-h leaching tests. Finally, the leaching ratio made little difference in the pH results as all of the leaching tests (excluding TCLP) produced a similar pH trend even though the paste pH test uses a 1:1 (leachant/sample) ratio and all of the other leaching tests use a 20:1 ratio. These findings indicate that the pH of the leachates was controlled by the highly reactive, readily soluble components of the samples, and verifies that short-term leaching tests are an effective tool to use to determine or predict the likely runoff (weathering pH) that metal mine waste samples will produce when leached by precipitation.

4.2. Leachate specific conductance

SC results for all 12 mine waste samples are shown in Fig. 2(b). SC data show that in general, the FLT 5-min, FLT 18-h, SPLP pH 4.2, and SPLP pH 5.0 leaching tests produced generally similar SC trends for all of the samples. However, SC data produced using the TCLP leaching test did not conform to this trend as it appears that SC in the TCLP leachates was overwhelmed and controlled by the ionic strength of the raw TCLP leachant. Because of this, the leachates were only minimally influenced by the actual concentration of soluble constituents leached from the samples. This is apparent as the TCLP SC results for most of the samples were more than an order of magnitude higher than SC results produced by the other leaching tests, and were found to be in the range of the

raw SC of the TCLP leachate (~4800 $\mu\text{S}/\text{cm}$). These results indicate that the TCLP should not be relied upon to characterize the leachable SC from metal mine waste. SC data from the other leaching tests showed that samples from TP1-N and TP1-S (high sulfide, low carbonate mineralogy) produced leachates with the highest conductivity. Whereas, the Ptarmigan mine waste (low sulfide and low to moderate carbonate mineralogy) produced the lowest overall leachate conductivity. SC could not be determined using the paste pH test because it did not produce any leachate. The most significant finding was that the use of DI water as the leachant and a 5-min agitation period produced SC results that were relative to those produced using the slightly acidified leachant and the 18-h agitation period.

4.3. Leachate element signatures

After analysis, the leachate data was synthesized and leachate geochemical trends showing selected major and trace elements for all samples are presented in Fig. 3(a)–(l). Complete leachate geochemical data (ICP-MS) for the samples are provided in SI Table 2.

The plots reveal that, in general, results from four of the five leaching tests produced similar leachate geochemical element trends for the samples. The exception once again was results produced using USEPA TCLP. The TCLP produced trends that were somewhat similar for the three most acidic leachates TP1-N, TP1-S, and Anvil-Faro but was inconsistent for the other, less acidic samples. For some elements, the TCLP produced results that were orders of magnitude higher for some elements. Other than TCLP results, the leachate geochemical profiles produced by the other leaching tests successfully revealed the geochemical signature of the water-reactive, water-soluble constituents of the samples. The leaching tests were also effective at grouping the samples

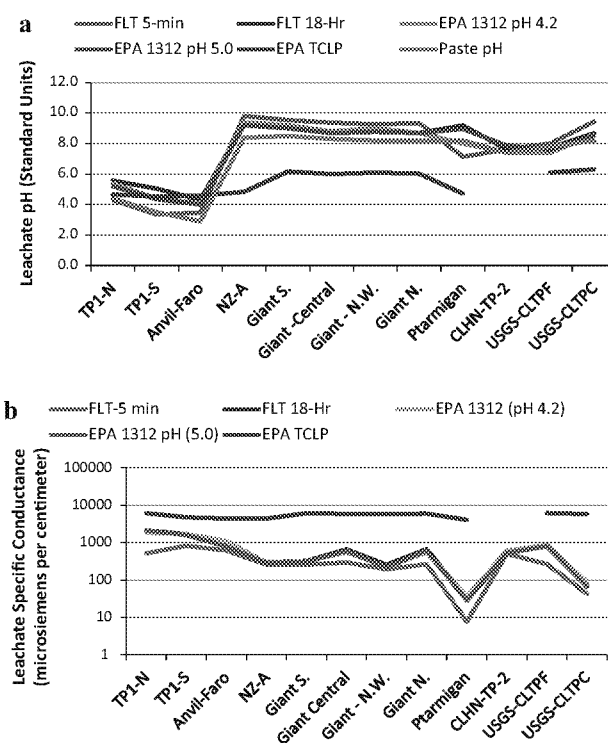
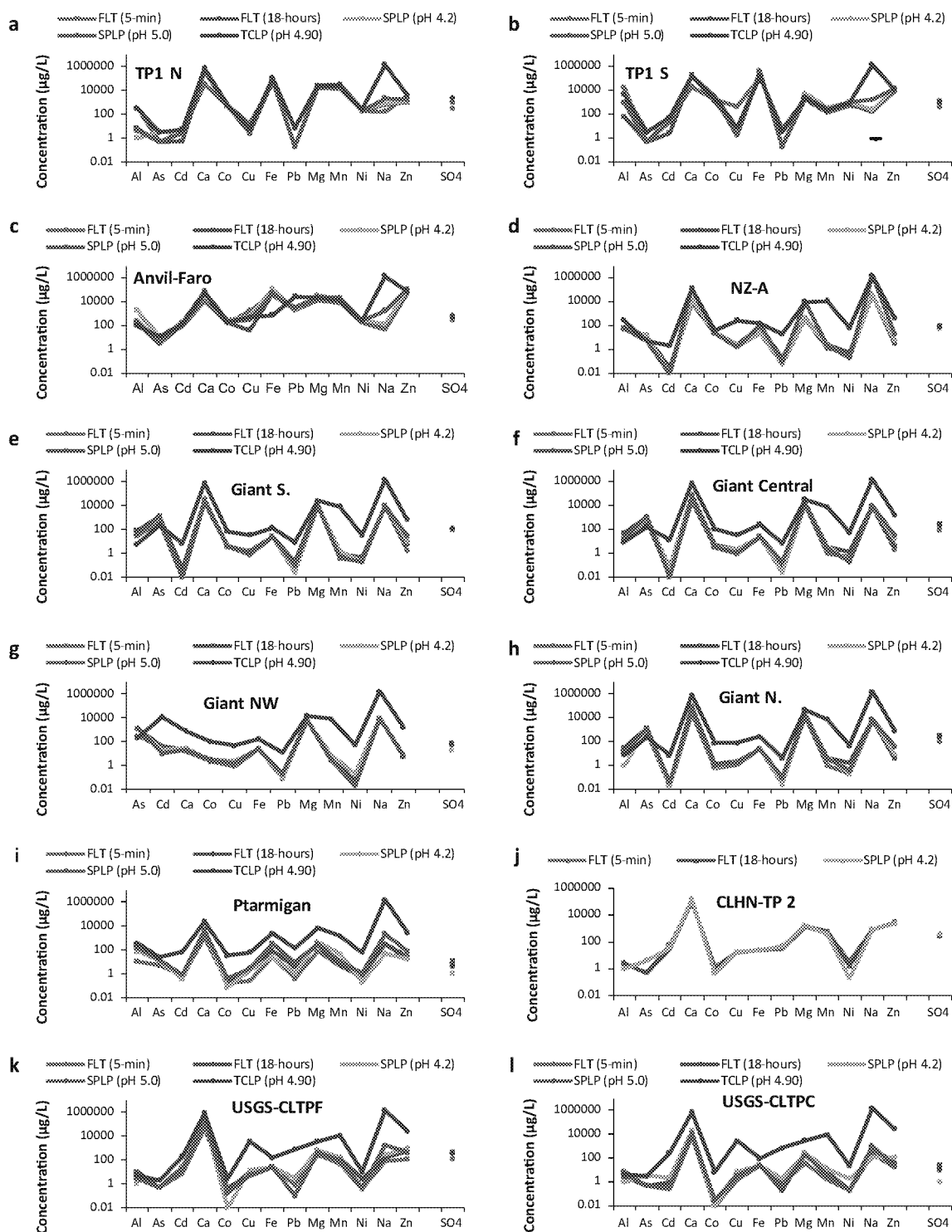


Fig. 2. (a) Leachate pH values for 12 mine waste samples using six leaching tests. (b) Leachate specific conductance values for 12 mine wastes using five leaching tests. (Sample without data was due to insufficient sample mass.)



*[All leaching tests could not be completed due to insufficient sample]

Fig. 3. (a)–(l) Leachate geochemical trends for selected constituents produced in leachates from five leaching tests. Elements are listed in alphabetical order. Note that there are no results from the paste pH test because it did not produce enough leachate for ICP-MS analysis. Also, only partial results are presented for sample CLHN-TP-2 because there was insufficient sample mass to complete all of the leaching tests.

according to deposit mineralogy characteristics. An example of this is shown in Fig. 4 in which the sum of selected metals (FLT 5-min) is plotted against leachate pH. Because all of the static leaching tests (except TCLP) produced similar leachate geochemical trends, they would all group the samples in a similar pattern as that shown for the FLT procedure in Fig. 4.

Overall, the leaching studies showed that while each mining waste produced different and unique leachate geochemical signatures, the intra-site samples collected from different areas of a specific mine site produced leachate signatures that were similar to one another (e.g., samples from the Callahan and Giant mines). This indicates that similar primary reactive minerals are present

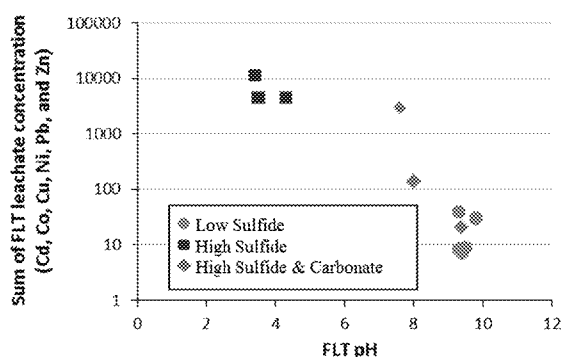


Fig. 4. Ficklin diagram showing that the sum of dissolved base metals (Zn, Cu, Cd, Pb, Co, and Ni) and FLT pH derived from leachates, effectively segregates the sample locations on the mineral deposit characteristics. The plot also shows that lower pH leachates contain the highest leachate concentration of metals, and that even wastes producing circum-neutral to slightly alkaline pH can contain significant metal concentration.

throughout the mine waste at these sites, and thus, similar soluble weathering salts and characteristics are developing at different locations on the mine waste piles. The results also show that the relatively simple USGS FLT (5-min) leaching test that uses deionized water and a short agitation time was just as effective as the tests that require acidified leachants and an 18-h agitation period to evaluate the leaching characteristics of metal mine waste samples. For the tests requiring an 18-h agitation, there was little difference in the leachate profiles produced using DI (FLT 18-h), or the slightly acidified pH 4.2 and pH 5.0 (SPLP). Inconsistent results produced by the TCLP show that it should not be used to characterize the leaching characteristics of metal mining waste.

4.4. Mineralogy results

Sample mineralogy determines and controls the composition of weathering salts, and thus, the mobilization of water reactive, water soluble constituents from mining waste into the environment. In the following summaries, we highlight the findings from the mineralogical examination of the samples, and show the connection between sample mineralogy and the unique and varied leachate geochemical signatures that were produced for each sample.

4.4.1. Elizabeth mine (TP1-N, TP1-S)

The mine waste is largely composed of grains of strain-shadowed quartz, albite (identified by XRD) and potassium feldspar, micas (muscovite and some biotite), chlorite, and lesser amounts of gypsum and hornblende. Feldspars are commonly partially altered to sericite and other clays. X-ray diffraction also identified talc and vermiculite. Reflected light examination shows that pyrrhotite is the most abundant sulfide in the Elizabeth mining waste. Other sulfide grains include minor chalcopyrite, pyrite, sphalerite, and galena. Pyrrhotite grains show a wide range of alteration textures—from grains with etched rims but fresh interiors, to fractured grains, to grains that are partially dissolved along fractures and rims, producing remnant “atoll” textures (Jambor, 2003, Fig. 5(A)). Many grains have undergone total dissolution and alteration to iron-oxide minerals and exhibit skeletal boxwork remnants. Partial to total dissolution textures in pyrrhotite grains (Fig. 5(B)) are evidence that constituents were taken into solution. Analysis by SEM/energy dispersive X-ray spectroscopy (EDS) shows that metals, such as zinc and nickel, are present in concentrations as high as 1 wt.% within pyrrhotite grains; therefore during weathering these metals are released into solution as are iron and sulfur.

Examination by SEM of mine waste grains shows that surfaces of sulfide minerals commonly have dissolution pits and are coated by aluminum–silica–iron precipitates that are host to copper, iron, and zinc (Table 3, Fig. 5(C)–(F)). Secondary oxidation alteration minerals that develop around sulfide grains, as well as amorphous coatings that precipitate from solution, can host metals (Diehl et al., 2007, Table 3). The aluminum–silica–iron coatings likely precipitated from pore waters as the mine waste dried (Jambor, 1994). These mineral coatings are amorphous to poorly crystalline and exhibit shrinkage cracking, which indicates that these coatings have been subject to wetting and drying events.

Fig. 5(F) is an SEM micrograph of a fragment of poorly crystalline alteration crust that lies directly atop the carbon surface of the SEM plug; therefore analysis by the microbeam is only penetrating the crust and not an underlying sulfide grain. Results show that such crusts are dominantly composed of aluminum, silica, and iron, but they also host metals such as Cu and Ni. Leachates, particularly the FLT (Fig. 3(A) and (B)), were unusually high in aluminum and iron indicating that the coatings are the probable source of these elements in leachates. Zinc was not identified at the detection limits of the SEM/EDS in the soluble amorphous coatings, but zinc was detected in iron-oxide alteration rims around sulfide grains, in skeletal iron-boxwork remnants (Table 3), and was present in the leachates. The Elizabeth mine waste produced very acidic leachate and the mobility of metals is increased at low pH, which is demonstrated by the elevated metal concentration of some metals in the leachate solutions.

4.4.2. Callahan mine (USGS-CLTPC, USGS-CLTPH, and CLHN-TP-2)

This mine waste is composed largely of quartz, albite (commonly partially altered to sericite), micaceous rock fragments, and calcite. In addition, talc, muscovite, hornblende, chlorite, and vermiculite were identified by XRD. Metal-sulfide minerals include pyrite, the predominant sulfide, sphalerite, chalcopyrite, and galena. In contrast to the low pH, aluminum- and iron-rich leachate solution from the Elizabeth mine waste sample, the iron concentration in more alkaline leachates from the Callahan mine waste sample is orders of magnitude lower (Fig. 3(j)–(l)). Many sulfide grains have amorphous to poorly crystalline coatings (Table 4).

These grains commonly exhibit secondary iron precipitates, which are rosette-like, low in Al, and do not exhibit shrinkage cracks related to wetting and drying (Fig. 6). Although the Callahan mine waste produced slightly alkaline leachate (pH ~ 8.0), acidic microenvironments are present at the surfaces of minerals, where sulfur- and Fe-oxidizing bacteria may flourish. The etch pits and the uniformity of size and morphology of the secondary mineral products are suggestive of precipitation/mineralization generated by sulfur-oxidizing microbes in laboratory studies (Edwards et al., 2001; Kawano and Tomita, 2001, Fig. 6(e)). Secondary precipitates commonly fill etch pits and coalesce into layers (Fig. 6(b)). As with the amorphous Elizabeth mine secondary-mineral coatings, it is difficult to determine the exact mineralogy of the micrometer-sized secondary phases that cover the sulfide grains. The secondary products commonly act as a binder between sulfide and other minerals, such as feldspar and chlorite grains in Fig. 6(d), but because these secondary phases are very fine grained and more susceptible to dissolution, they make unstable weak cements between grains.

4.4.3. Newmont Martha mine (NZ-A)

These mill tailings are largely composed of quartz and sanidine (identified by XRD) with pyrite, albite, muscovite, chlorite, and lesser amounts of manganese-, iron-, and titanium-oxides, kaolinitic and illitic clays, minor to sparse carbonate fragments and chromium-bearing spinels. Thin section analysis shows that metal-sulfide minerals are finer grained, more euhedral, and less liberated from surrounding minerals, such as quartz and feldspar, than sul-

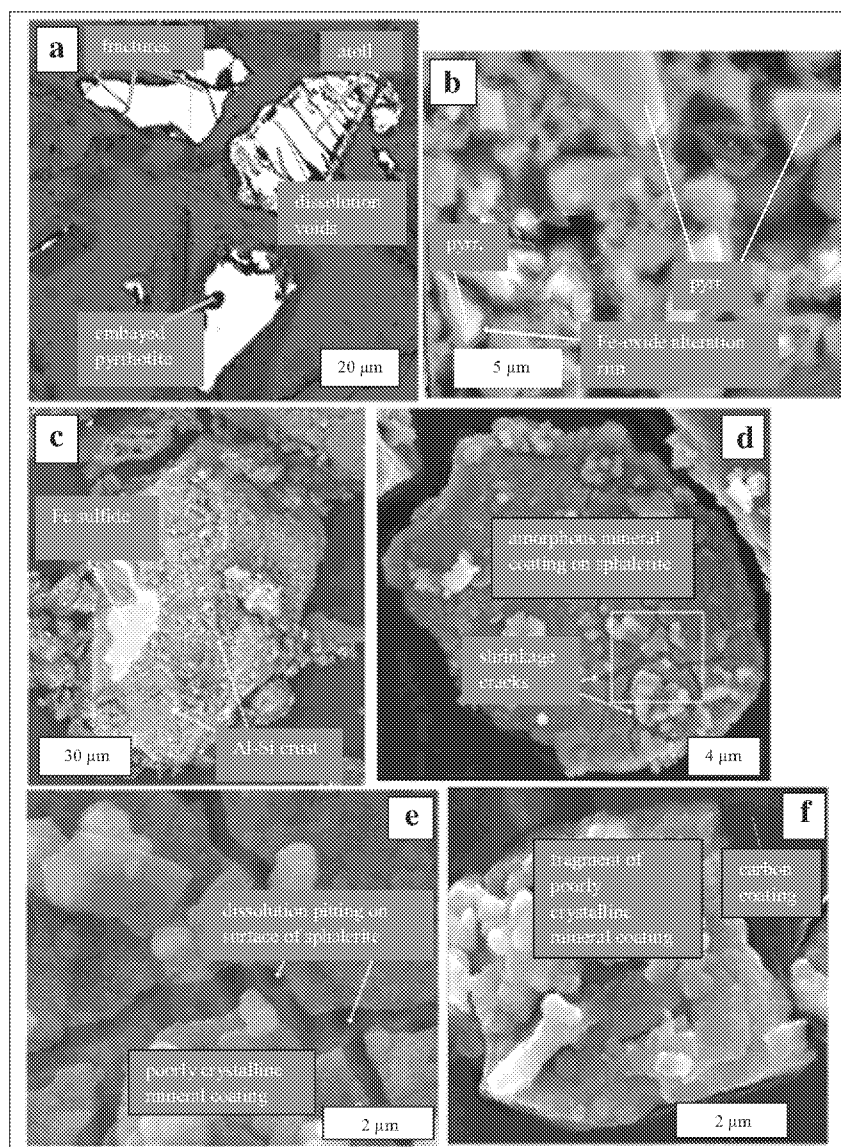


Fig. 5. Alteration of sulfide grains in mine waste, Elizabeth mine, Samples TP1-N and TP1-S. (a) Reflected light micrograph of pyrrhotite grains, collected from surficial mine waste, shows varying degrees of alteration. (b) SEM photomicrograph of polished thin section surface of pyrrhotite with alteration rims of iron oxides. (c) Backscatter micrograph of sulfide grain coated by aluminum-silica-iron secondary minerals. Bright area is the etched surface of the sulfide. (d) SEM photomicrograph of sphalerite grain coated by secondary amorphous minerals, which likely precipitated by dehydration of pore fluids. Dehydration is also responsible for development of the shrinkage cracks. Area outlined in the white square is depicted in (e). (e) Close-up SEM micrograph of: (1) dissolution etch pits in surface of sphalerite, (2) poorly crystalline mineral coating, and (3) shrinkage cracking. Lack of crystallinity demonstrates rapid precipitation of these secondary mineral coatings during drying cycles. (f) SEM micrograph of fragment of amorphous secondary mineral crust which are host to elements such as Cu, Ni, and Zn.

Table 3

Semi-quantitative EDS analysis of secondary Fe-oxide alteration rinds around sulfide grains from Elizabeth mine waste [Elizabeth mine = Samples: TP1-N and TP1-S].

Locality/sample	O (wt.%)	Na (wt.%)	Mg (wt.%)	Al (wt.%)	Si (wt.%)	S (wt.%)	K (wt.%)	Ca (wt.%)	Fe (wt.%)	Ni (wt.%)	Zn (wt.%)
Elizabeth mine; Fe oxide rinds	36.0	0.62	0.41	1.10	1.90	6.30	0.73	BD	52.9	BD	BD
Elizabeth mine; Fe oxide rinds	39.4	0.38	BD	1.20	3.70	9.70	0.30	0.22	44.5	0.40	0.26
Fe oxide boxwork	31.1	BD	BD	0.79	0.75	BD	BD	BD	63.5	BD	2.80

wt.% = weight percent; BD = below detection.

fides from the other sites (Fig. 7(a)). SEM analyses of grains show aluminum-silica-iron crusts with high chlorine content that partially coat liberated euhedral sulfide grains, which range from approximately 5 to 10 μm in diameter. Larger sulfide grains up to 25 μm in diameter show extensive fracturing. Mine waste from NZ-A produced the highest leachate pH (9.8), which can be

explained by the presence of carbonate minerals and by the encasement of metal-sulfide minerals within silicate minerals. Leachate produced from this material contained moderately elevated concentration of the major-elements sodium and magnesium, elevated concentration of the trace metal arsenic, and slightly elevated concentration of aluminum.

Table 4

Semi-quantitative EDS analysis of amorphous to poorly crystalline Al–Si–Fe mineral coatings on sulfide grains from selected samples.

Locality/sample	O (wt.%)	Mg (wt.%)	Al (wt.%)	Si (wt.%)	S (wt.%)	Cl (wt.%)	K (wt.%)	Ca (wt.%)	Fe (wt.%)	Cu (wt.%)	Ni (wt.%)	Zn (wt.%)
TP1-N, TP1-S; Al–Si–Fe crust	43	BD	10	7.3	8.7	BD	0.70	BD	29	1.3	BD	BD
TP1-N, TP1-S; Al–Si–Fe crust	44	BD	11	7.6	9.7	BD	BD	BD	28	BD	BD	BD
TP1-N, TP1-S; Al–Si–Fe crust	40	5.1	2.2	4.2	10	3.7	BD	5.3	28	1.6	BD	BD
CLTPC ^b , CLTPH ^b , CLHN-TP-2 ^b ; Al–Si–Fe crust	43	7.2 ^a	3.2	4.3	13	BD	BD	0.2	26	1.4	BD	2.0
CLTPC ^b , CLTPH ^b , CLHN-TP-2 ^b ; secondary minerals	46	BD	0.20	0.20	21	BD	BD	BD	29	BD	BD	3.6
Anvil-Faro ^b ; Al–Si–Fe crust	47	BD	6.5	7.7	17	BD	BD	BD	8.7	BD	BD	13
Anvil-Faro ^b ; Al–Si–Fe platy crust	42	BD	3.3	2.4	14	BD	BD	BD	38	BD	BD	1.2
Ptarmigan Al–Si–Fe platy crust	41	6.7	4.0	15	BD	1.0	2.4	8.8	16	BD	BD	5.4

wt.% = weight percent; BD = below detection limit or not detected.

^a Beam penetrated nearby chlorite flake (?).^b Beam analysis influenced by proximity of sulfide grain but important to note the presence of an amorphous Al–Si coating.

4.4.4. Anvil-Faro mine (Anvil-Faro)

Quartz, muscovite, micaceous rock fragments, and sulfide minerals are abundant in the mine waste. Metal-sulfide grains are pyrite, chalcopyrite, sphalerite, pyrrhotite, and galena (Fig. 7(b)–(f)). Jarosite, kaolinite, and marcasite were identified by XRD. Jarosite forms under acidic conditions (pH 1–3), therefore low pH and high metal concentrations were expected in the leachate solutions.

Excluding TCLP results, the Anvil-Faro produced the lowest leachate pH values and the highest leachate lead concentration at about 2900 µg/L and zinc at 130,000 µg/L (Fig. 3(c), SI Table 2); SEM examination showed that this mine waste sample had the largest galena grains of all the sites. Galena is commonly partially altered to anglesite at the grain rims as well as along fractures (Fig. 7(e) and (f)).

Anglesite forms a rim of varying thickness around grains, penetrating into galena grains along cracks (Fig. 7(f)). Anglesite shows dissolution textures, especially in pitting along the reaction front adjacent to the galena grain. Studies have demonstrated that anglesite is soluble at ≤3.5 pH (Desborough and Fey, 1997), which is the approximate pH of the leachate solutions. EDS mineralogy results for Anvil-Faro amorphous secondary mineral crusts are provided in Table 4.

4.4.5. Giant mine (Giant NW, Giant N, Giant Central, and Giant S.)

Minerals in the mine waste identified by XRD are quartz, chlorite, dolomite, muscovite, albite, gypsum, and calcite; metal-sulfide minerals identified in the mine waste by reflected light microscopy and SEM include pyrite, arsenopyrite, sphalerite, chalcopyrite, and pyrrhotite grains. Mine waste from the Giant site produced slightly alkaline pH and the highest concentration of arsenic in the leachates (Fig. 3(e)–(h), SI Table 2). Arsenic occurred originally in primary pyrite and arsenopyrite, but due to weathering it is now concentrated in iron-oxide alteration rinds (Fig. 8(a) and (e)), which is a result of ore processing and roasting methods (Walker and Jamieson, 2005).

All the altered iron-sulfide grains that were examined showed an increase in arsenic concentration from the core of the grain to the iron-oxide alteration rims. For example, the core of the iron-sulfide grain in Fig. 8(a) has approximately 1 wt.% arsenic, whereas the rim contains approximately 8 wt.% arsenic. Similarly, the core of the Fe-sulfide grain in Fig. 8(b) has approximately 0.5 wt.% arsenic, whereas the alteration rinds host up to 6.5 wt.% arsenic. A series of element intensity maps of the grain in Fig. 8(b) shows the distribution of sulfur, iron, and arsenic. High density areas of a color record the highest concentration of the element, and Fig. 8(e) shows that the highest concentration of arsenic is in the poorly crystalline Fe-oxide rinds. Arsenic may be sorbed onto the surfaces of the iron-oxides that occur within the structure (Walker and Jamieson, 2005).

4.4.6. Ptarmigan mine

Mine waste grains are mostly strain-shadowed quartz, with minor feldspar (identified as albite by XRD), micas such as phlogopite, chlorite, and rare amphibole and carbonate grains. Metal-sulfide minerals include pyrite, sphalerite, and galena with minor chalcopyrite and pyrrhotite. Iron-sulfide grains exhibit dissolution textures and alteration to iron oxides (Fig. 8(f) and (g)). Reaction fronts between iron sulfide and secondary iron oxides are penetrative (arrows in Fig. 8(f)). The leachate solutions produced were circum-neutral to alkaline, but arsenic and metals such as cadmium, manganese, lead, and zinc occur in the leachate solution (Fig. 3(i), SI Table 2).

Euhedral metal-sulfide grains are commonly coated with aluminum-rich amorphous material (Table 4) and clays. In addition to the chemical reactions and changes that occur, physical transformations such as fracturing and resulting comminution of grains are typical and were observed in all the mine waste samples. A physical change such as reduction in grain size is important because of increased chemical reactivity with decreasing grain size, due to higher surface area to unit mass (Fig. 8(g)).

4.4.7. Mineralogy Summary

The mineralogical studies verified the presence of readily soluble, metal-rich secondary phases and showed that amorphous, poorly crystalline coatings are the primary source of characteristics and constituents found in the leachates. The studies verified the formation of alteration minerals (e.g., anglesite around galena), which confirmed that acid producing and acid attenuating processes are occurring in situ due to weathering. Mineralogical examination also showed that acidic microenvironments exist at the surfaces of metal-sulfide minerals, where biotic weathering processes including sulfur- and iron-oxidizing microbes may be active at the reactive mineral-biofilm interface. This finding helped explain why even though the mobility of metals is often increased at acidic pH, many of the mine waste samples with circum-neutral to basic pH also yielded leachates with high concentrations of metals (e.g., Fig. 4, SI Table 2). Examination of the mineralogy and weathering features in the mine waste samples was useful in verifying and understanding the mineralogical characteristics that control the reactivity and release of soluble constituents from the waste materials. SEM visualization of the textures caused by weathering processes also showed how the reservoir of metal-sulfide minerals still present in the mining waste will continue to be a long-term, ongoing source of metals in leachate produced from the mining waste.

4.5. Acid-base accounting results

For the ABA comparison study, all the samples were analyzed using both traditional and simplified ABA methods.

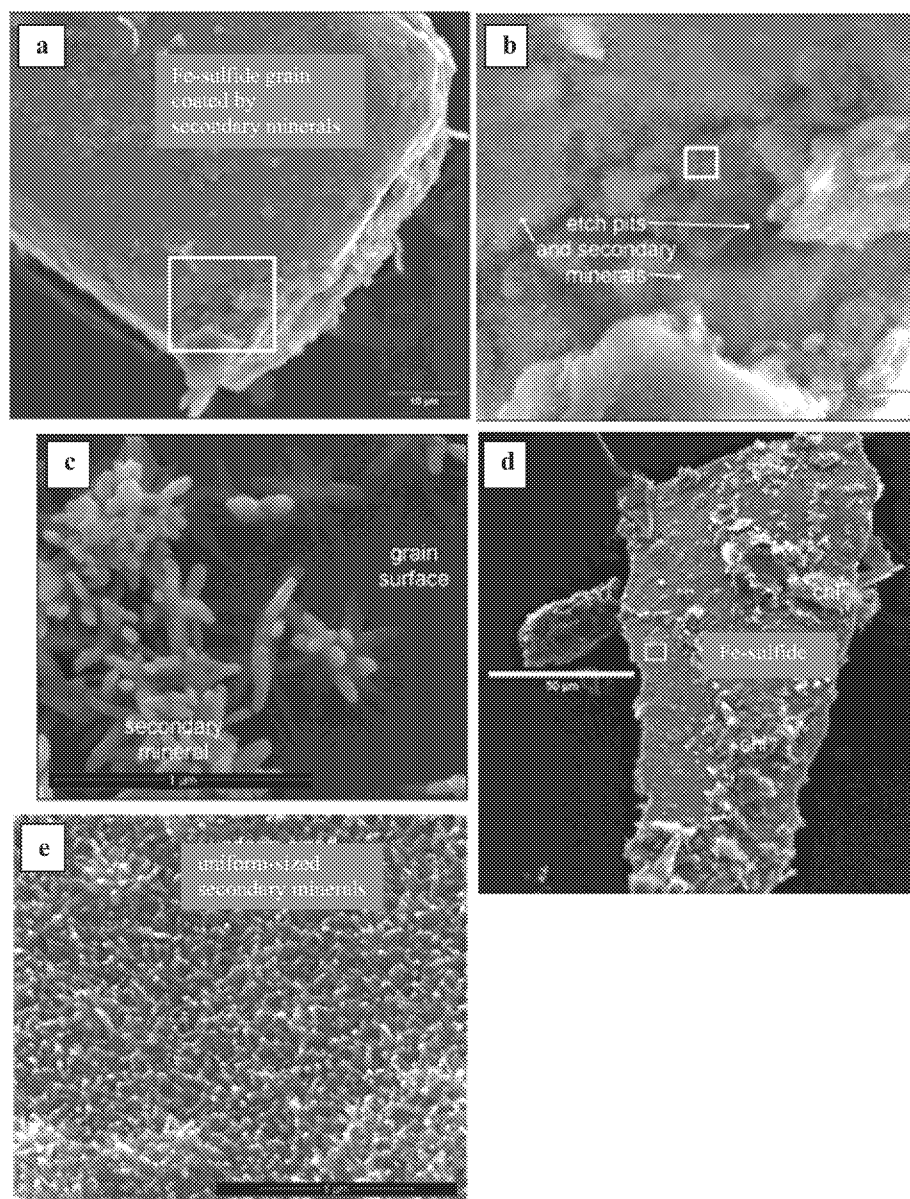


Fig. 6. Alteration of sulfide grains, Callahan mine, Samples: USGS-CLTPC, CLHN-TP-2, and USGS-CLTPF. (a) SEM micrograph of Fe-sulfide, probably pyrite, coated by secondary minerals. White square is area depicted in (b). (b) SEM micrograph showing a close-up of etch pits in sulfide grain and secondary minerals that form a dense network on the sulfide grain. (c) SEM micrograph showing an enlarged area (white square in (b)) of secondary mineral growth on surface of sulfide grain. (d) Sulfide grain coated by similar alteration mineralogy observed in (a)–(c). (e) SEM micrograph of close-up (area depicted by white rectangle in (d)) of very fine-grained uniformly shaped secondary mineral products, iron sulfates and/or iron-oxide (oxyhydroxide) mineral coating. The secondary mineral product may be generated by microbial activity because it is not a well-ordered crystalline mineral, and it is of uniform size and shape, typical of microbial mineral products (e.g., Edwards et al., 2001).

Complete results from the comparison study are presented in Table 5.

Evaluation of the ABA results produced several interesting conclusions. First, results from the traditional ABA studies showed that the highest AP values were produced by the Anvil-Faro mine waste followed by TP1-N and TP1-S. These three samples also had the highest total sulfur values and produced the lowest leachate pH values. The highest NP values were produced by the mine waste samples produced from the Giant mine waste, which also produced some of the lowest total sulfur and highest, most alkaline leachate pH values. These results indicate that the propensity for the samples to produce acid in the leachate is controlled by the relative abundance or absence of sulfide and carbonate minerals in the mine waste. The data also showed that for the most part, the relatively simple NABA method was quantitatively as effective as the

traditional methods in identifying the mine waste samples that produce acid. For this comparison, we categorized net acid-generating samples as those that produce calculated NNP values <0 kg CaCO_3/t and compared those results to results produced using the NABA test. The comparison showed that the simplified NABA procedure correctly identified five out of six of the net acid-producing samples that had negative NNP values using the traditional test (Table 5). The traditional NNP method predicted the USGS-CLTPF sample as slightly acid generating (-62.7 kg CaCO_3/t), whereas the NABA procedure failed to classify the USGS-CLTPF sample as acid generating, classifying it instead as net-neutralizing. This deviation is likely due to unusual characteristics of the USGS-CLTPF sample when compared to the other two samples collected at the Callahan mine site (USGS-CLTPC and CLHN-TP-2). This is confirmed by the ABA results (Table 5), which show that the

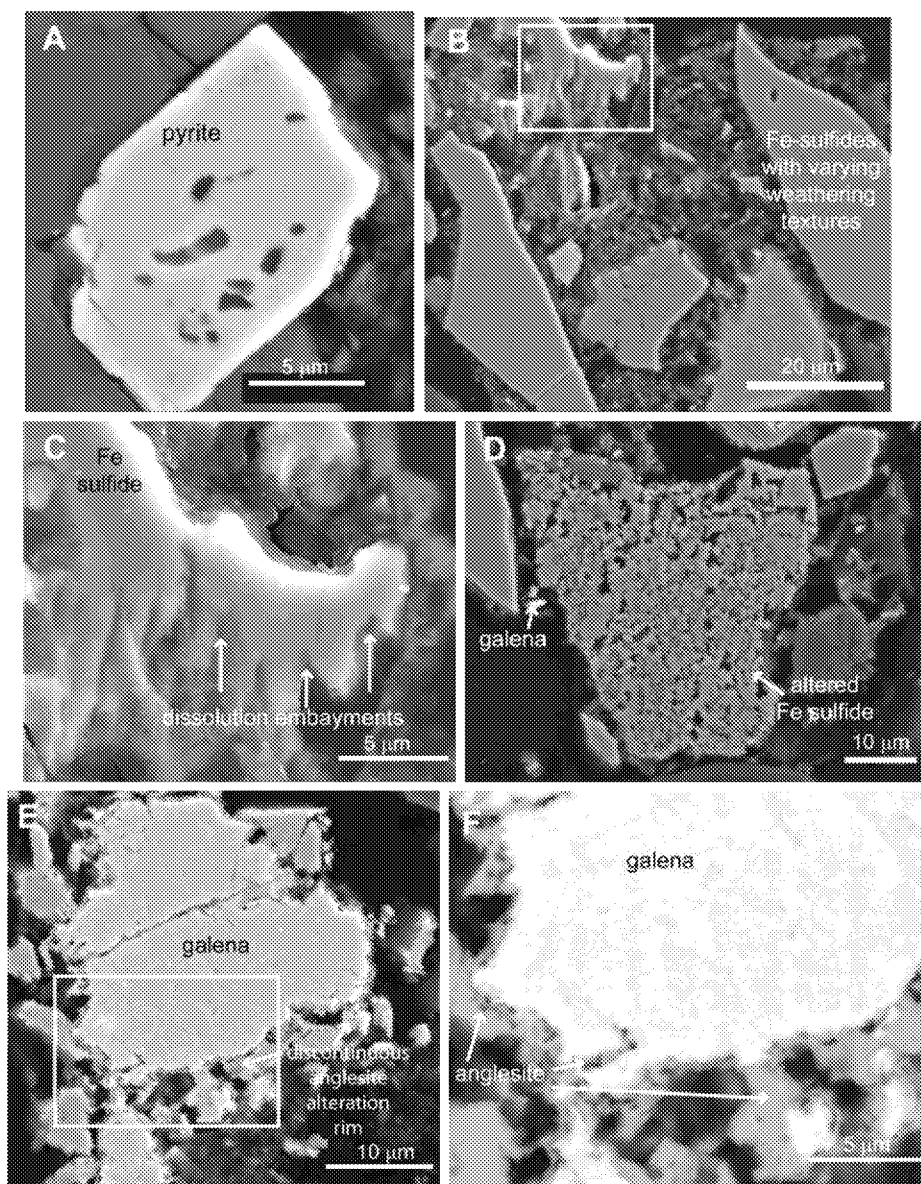


Fig. 7. Newmont Martha mine, Sample: NZ Newmont A (a). (a) SEM micrograph of euhedral pyrite, with a porous texture, encased in quartz. Anvil-Faro mine, Sample: Anvil-Faro. (b) SEM micrograph showing Fe-sulfide grains with varying degrees of weathering textures, from a deeply etched grain (white rectangle) to grains with fresh fractured surfaces. Area of white rectangle is depicted in (c). (c) SEM micrograph of etched Fe-sulfide grain, deeply embayed by dissolution and coated with clay minerals. (d) SEM micrograph of altered and pitted grain-size remnant of a Fe-sulfide grain. (e) Galena is common in the Anvil-Faro mine waste. The galena grains show dissolution etching, and alteration to anglesite around the rims, penetrating along fractures. (f) Backscatter SEM micrograph of area in white rectangle in (e), showing bright galena (PbS) and dull gray anglesite (PbSO₄). Note that the anglesite is pitted, especially adjacent to the galena, and does not form a uniform thickness coating.

USGS-CLTPF sample has much higher AP and much lower NP than the other two Callahan mine waste samples. These data show that for an unknown reason the USGS-CLTPF sample had a larger ratio of metal sulfides to carbonate minerals in the sample split sent to the labs that determined NNP. Results from the Fizz Test also indicate that all three Callahan samples produced a “strong” fizz rating indicating that all three samples had carbonate or strong acid buffering mineralogy. Like the NABA test, the Fizz Test correctly categorized all the acid producing samples except the USGS-CLTPF sample. As for the NABA results, it is important to note that this procedure does not quantify the total neutralization potential, but only indicates the samples that are “net neutralizing.” Net neutral samples are identified with “0” in the NABA column in Table 5. Regardless of the lack of quantification of the total NP, NABA results are still meaningful because they indicate whether a sample has net-acid or net-neutralizing weathering

mineralogy, and thus whether a mining waste has the potential to produce or consume acid.

Overall, comparison of the methods showed that the traditional ABA methods provide a plethora of data, and more in-depth quantification of the AP and NP components of the sample. However, these methods are very time consuming to conduct and require expensive instrumentation. Rapid estimation of the ABA for weathered metal mine waste can be achieved using the simplified NABA procedure.

4.6. Using leachate pH to indicate the net acid–base characteristics of weathered mine waste samples

While leachate pH from any of the leaching tests (excluding TCLP) can be used to predict the likely net ABA propensity of weathered mine waste samples, the comparison study showed that

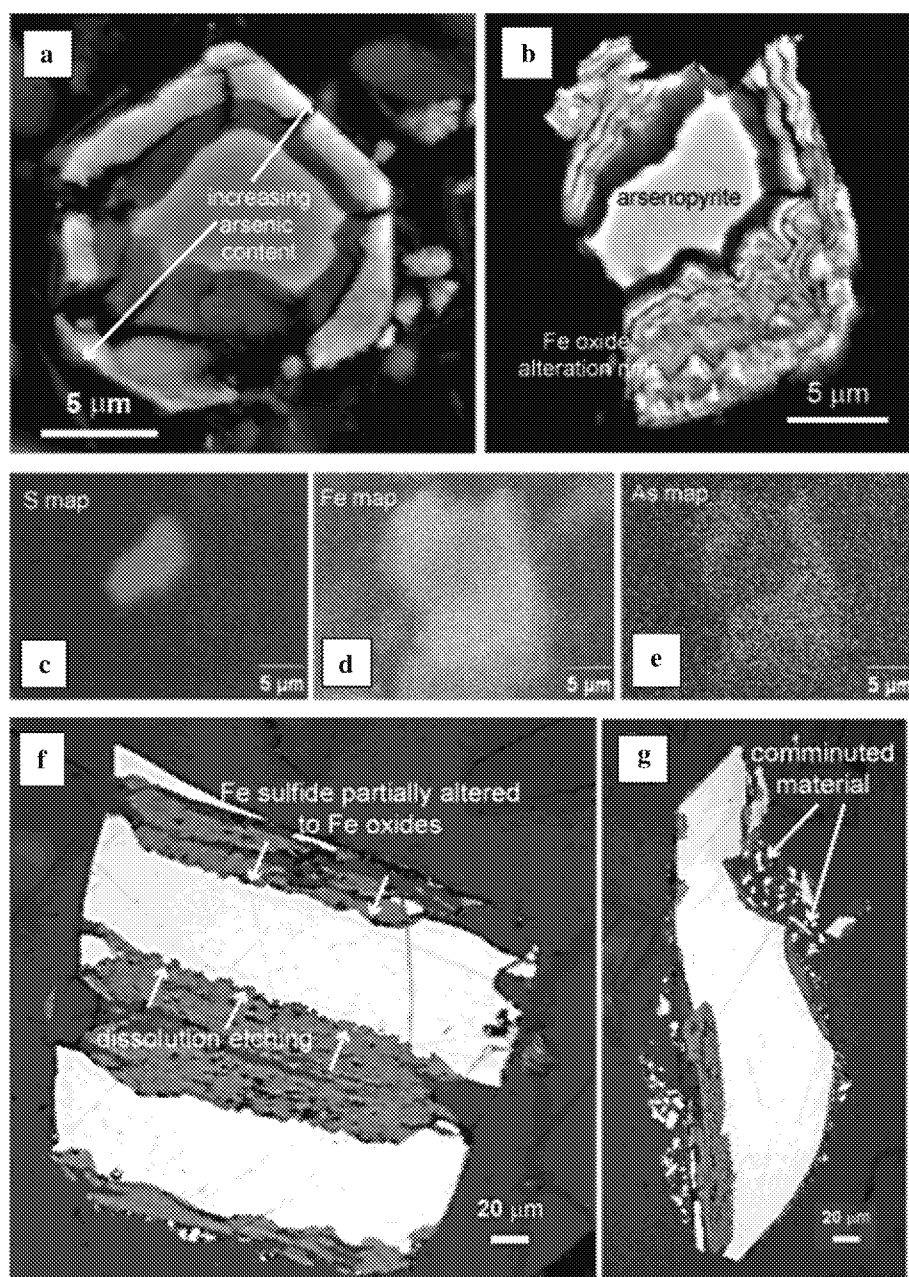


Fig. 8. Giant mine, Samples: Giant-NW, Giant-North, Giant-Central, and Giant-South (a)–(e). (a) Iron sulfide partially altered to arsenic-bearing iron oxides; arsenic content radially increases to outer rim. (b) Dissolution etched, altered arsenopyrite with As-bearing Fe-oxide rinds. (c) Sulfur element intensity map of grain depicted in (b), showing sulfur-rich core of grain. (d) Iron element intensity map of grain depicted in (b). Dense areas of green show higher iron content in the alteration rinds than in the core grain. (e) Arsenic intensity map of grain depicted in (b). Dense areas of blue show higher arsenic concentration in alteration rinds. Ptarmigan mine, Sample: Ptarmigan (f and g). (f) Reflected light micrograph of iron-sulfide grain partially altered to iron-oxide minerals. Note dissolution etching along alteration fronts (white arrows). (g) Reflected light micrograph of sulfide grain. Weathering not only involves chemical changes to form secondary minerals, but physical changes such as comminution of grains, which increases the surface area of particles to reactions with fluids and oxygen.

because of the short agitation time required for the FLT (5-min) procedure, it provides the fastest method to use for this purpose. The effectiveness of using FLT pH is possible because for weathered metal mining waste, the kinetic rate of reaction and interplay of all the minerals present in the mining waste has been determined, controlled, and completed over time as a result of natural, site specific weathering processes. The FLT is effective because it rapidly dissolves these readily soluble phases providing a snapshot of the net or “weathering” ABA of the mine waste materials. Whereas other studies (Hughes et al., 2006; Weber et al., 2006) have previously shown that pH results from the paste test provide indication

of short-term ABA potential of a mine waste sample, this study provides data showing that the use of either paste pH or 5-min FLT pH are effective at predicting not only the short-term, but also the long-term ABA behavior of weathered metal mining waste.

The effectiveness of the FLT leaching test in revealing the weathering ABA characteristics of metal mine waste samples is easier to understand when we see that pH data produced using the paste pH test and the FLT (5-min agitation) correlate reasonably well with the NABA digestate liquor pH trend which was derived after completion of the 150 mL hydrogen peroxide-digestion (prior to titration) (Fig. 9).

Table 5

Results from comparison study of acid–base accounting (ABA) methods using different procedures [data produced using simplified tests in italics; total sulfur and sulfate sulfur given in wt.%, weight percent; acid production (AP), neutralization potential (NP), net neutralization potential (NNP), and the net acid–base account (NABA) data given in kg CaCO₃/t, kilograms CaCO₃ per ton; NABA data converted to negative values for comparison; <, less than].

Mine waste sample	Paste pH	FLT pH	Post peroxide digestate pH	Total sulfur	Sulfate sulfur	Sulfide sulfur*	AP**	NP	NNP	NABA	Fizz test
TP1-N	4.4	4.3	1.9	12.10	1.39	10.71	334.7	10.7	–324.0	–127	None
TP1-S	3.5	3.4	1.8	9.58	1.16	8.42	263.1	–19.4	–282.5	–193	None
NZ-A	8.4	9.8	3.3	0.70	0.07	0.63	19.7	9.0	–10.7	–4	None
Anvil-Faro	2.9	3.5	1.7	22.50	0.97	21.53	672.8	–15.0	–687.9	–316	None
Giant S.	8.5	9.5	8.9	0.23	0.08	0.15	4.7	216.7	212.0	0	Strong
Giant Central	8.3	9.4	8.3	0.41	0.20	0.21	6.6	253.5	246.9	0	Strong
Giant N.W.	8.2	9.3	9.4	0.44	0.04	0.40	12.5	187.2	174.7	0	Strong
Giant N.	8.2	9.3	9.9	0.32	0.19	0.13	4.1	193.5	189.4	0	Moderate
Ptarmigan	8.2	7.1	4.0	0.21	<0.01	0.21	6.6	4.6	–1.9	–2.5	None
CLHN-TP-2	7.4	7.6	9.3	1.76	0.17	1.59	49.7	122.5	72.8	0	Strong
USGS-CLTPF	7.8	8.0	7.2	4.27	0.29	3.98	124.4	61.7	–62.7	0	Strong
USGS-CLTPC	8.2	9.4	9.0	3.17	0.01	3.16	98.8	140.2	41.4	0	Strong

Note: 1

*Based on difference between total sulfur and sulfate sulfur.

**Based on sulfide sulfur.

Total Sulfur by LECO furnace.

Note: 2

NP Method Used: Modified ABA Method (Lapakko and Lawrence, 1993).

Note: 3

Custom SO₄-S extraction was performed as per SOP 7410 but with the following changes:

- (1) Used 2.0 g of pulp sample instead of 5.0 g.
- (2) Used concentrated HCl instead of 3 N HCl.
- (3) Extended boiling time to 10 min instead of regular 1–2 min.

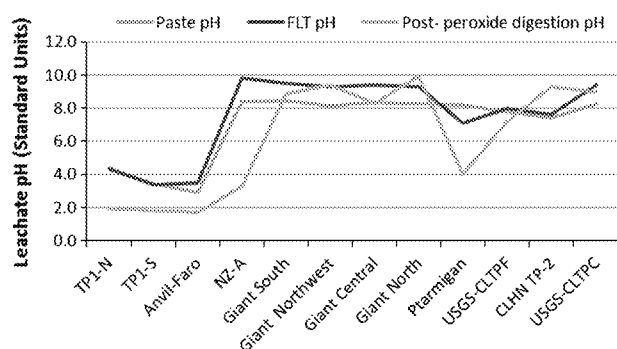


Fig. 9. Plot comparing pH trend of Paste pH and the FLT (5-min) leachate pH to the post-peroxide digestate pH.

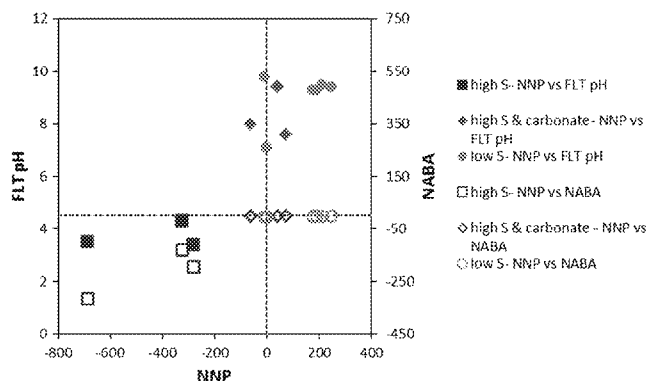


Fig. 10. Plot comparing results produced using FLT pH (5-min) and the NABA test to NNP results produced using traditional ABA procedures. The plot shows that both the FLT and NABA procedures easily segregate samples with acid producing mineralogy from those with acid consuming and mixed mineralogy. Note that the NABA procedure does not quantify the total acid neutralizing capacity of the samples but only quantifies the samples as net-neutralizing.

These findings show that for 10 of the 12 samples, the acid-producing (metal sulfides) and acid-neutralizing minerals (carbonates and silicates) must have already reacted in situ, leaving minimal unreacted minerals available in the waste to be digested by the peroxide. This confirmed that as a result of weathering reactions, the primary acid producing and/or acid buffering characteristics of the mining waste are close to steady state and now reside as readily soluble phases in the secondary salts. For most of the samples included in this study, digestion with 150 mL peroxide did not make a significant difference in the pH trend of the relative to those produced by the Paste pH test or the FLT (Fig. 9). One of the samples that did not fit the correlation was the NZ-A sample. The reason for the much lower post-peroxide digestion pH for this sample is due to the fact that it was collected from un-oxidized mill tailings and not from weathered mining waste like the other 11 samples. This sample was not weathered and thus, there was higher proportion of metal sulfides available for digestion by the peroxide. Subsequent peroxide oxidation and reaction of the sulfides significantly lowered the peroxide digestate pH of the NZ-A sample. This finding shows the importance and efficiency of the natural weathering process in the physical breakdown and reaction of the primary minerals in situ.

The effectiveness of using the leachate pH to estimate the weathering acid–base tendency of mining waste can be taken a step further. This study shows that FLT leachate pH can also be used to estimate the final NNP trend of the samples. Fig. 10 shows a comparison of final NNP (kg CaCO₃/t) produced using the traditional methods, net NNP produced using the simplified NABA procedure, and leachate pH produced using the 5-min FLT. In this study, samples with NNP values <0 are considered net acid producing. For the FLT, samples producing leachate pH values <4.5 are considered acid producing.

Fig. 10 shows that FLT pH and the NABA procedure are reasonably effective at identifying the samples that are net-acid producing or net acid neutralizing. While traditional methods do provide more information on forms of sulfur along with separate quantification of the acid producing (AP) and the neutralization potential (NP), the net acid–base propensity of the mine waste samples could be estimated using either FLT pH or NABA test. This is

Table 6
Selected leaching results, characteristics, and capabilities for the static leaching tests compared in this study. Tests include: Paste pH, the U.S. Geological Survey (USGS) Field Leach Test (FLT) (both 5-min and 18-h agitation) and modified versions of the U.S. Environmental Protection Agency (USEPA) Method 1312 (SPLP) (both pH 4.2 and pH 5.0 leachates), and the USEPA Method 1311 (TCLP) [SC = Specific Conductance].

Characteristic	Paste pH	USGS FLT (5-min)	USGS FLT (18-h)	USEPA 1312 SPLP	USEPA 1311 TCLP
Produced relative pH trend for samples	X	X	X	X	
Produced relative SC trend for samples		X	X	X	
Produced enough leachate for all analysis		X	X	X	X
Produced relative leachate geochemical results		X	X	X	
Uses short duration agitation (<18 h)	X	X			
Procedure is a regulatory test				X	X
Method is relatively simple and can be used either in situ or in the laboratory	X	X			

remarkable given that obtaining FLT pH takes 5 min and both the traditional methods and the NABA procedure require considerably more time, effort, and expense in order to determine the ABA. These results show that the natural weathering process has effectively digested the mining wastes in situ making available readily soluble, end-state weathering products.

5. Conclusion

This study compared and evaluated commonly used static leaching and acid–base accounting tests on geologically diverse, modern-style metal-mining wastes. The static tests included both traditional and simplified methods. Comprehensive mineralogical studies were conducted in order to confirm the relationship between mineralogical characteristics, weathering features, leachate geochemical signatures and ABA characteristics produced by the samples.

The comparison of static leaching tests showed that all the leaching tests provided comparable leachate geochemical characteristics and trends for the samples except the EPA TCLP (1311) method. The TCLP did not produce consistent leachate geochemical results when compared to results produced using the other leaching tests. In some cases, the TCLP leachate concentration of some elements were multiple orders of magnitude different than results produced by the other leaching tests. The TCLP also produced leachate pH and specific conductance trends for the samples that were significantly different from trends produced by the other tests. These results confirmed that the TCLP was not designed nor should it be used to characterize water-induced runoff from metal mining waste. Other results showed that mine waste samples from different deposits produced leachates with different and unique geochemical signatures, whereas mine waste samples collected from the same deposit produced similar leachate geochemical signatures. Other comparisons showed that the relatively simple deionized water-based FLT (5-min agitation) was just as effective as the other leaching tests that required acidified leachants and 18-h agitation to characterize the pH and the geochemical signature of metal mining waste. Also, because of the short agitation period and use of DI water required by the FLT, results produced by this test provide the most realistic estimation of the likely runoff pH that would be mobilized from mining waste as a result of natural precipitation events. Excluding the TCLP, the other leaching tests were equally effective at revealing the water soluble phase of the samples but require a much longer agitation period than is necessary. Table 6 provides an overview of selected results, characteristics, and capabilities of the leaching tests used in this study.

The comparison of traditional and simplified static acid–base accounting methods showed that the value of using the simplified NABA method to provide the “net” ABA characteristics of the samples. Traditional ABA methods provide the most in-depth information about the samples including the forms of sulfur, and separate

AP and NP characteristics. However, the comparison showed that for weathered metal mining waste the use of complex, time consuming traditional ABA analyses and methods were not necessary in order to estimate whether the sample would produce or consume acid.

The use of pH values produced from the Paste pH test and FLT (5-min) leaching test produced similar ABA trends for the samples as those produced by the simplified NABA procedure and the traditional ABA procedures. However, the advantage of using the FLT for this purpose is that it provides enough leachate for all the desired analyses, whereas the paste pH test does not provide any leachate for analysis.

In-depth mineralogy studies verified the reasons for the effectiveness of the simplified tests, as minerals from all of the sites exhibited various degrees of oxidation and dissolution. Features such as dissolution-etched grain rims, complex rinds of secondary minerals, and skeletal remnants of metal-sulfide grains are all evidence of long-term, in-situ reaction of acid producing and acid consuming minerals in the mining waste. Over time these reactions produced end-stage, readily soluble weathering products that upon dissolution revealed both the current leachate geochemical signature and the weathering ABA of the material.

Ultimately, this study showed that traditional static methods, while perfectly effective, do not necessarily provide better estimation of the leaching and net acid–base characteristics of the samples than are provided by the simplified procedures. Traditional methods are still best for regulatory and modeling purposes. However, using a combination of simplified methods such as the FLT and NABA procedures provide effective tools to quickly assess the leaching potential and net acid–base account of modern-style weathered metal mining waste.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apgeochem.2014.12.007>.

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